Abstract No: crof509

XAS Studues of the La₅(Mo,Co)₄O₁₆ System

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Beamline(s): X19A, X18B

 $La_5(Mo,Co)_4O_{16}$ is a quasi-2-D compound containing perovskite-like MoO₃, layers sandwiched between Mo₂O₁₀ insulating clusters. Co substitution in this material occurs at the perovskite sites. In Figure 1 we show Co-K edge XAS measurements for $La_5Mo_3CoO_{16}$ along with Co-standards. The coincidences between the Co^{2+} standard and the Mo/Co-compound spectra at the edge-onset energy (see box 1 in the figure) and the steeply rising portion of the edge energy (see box 2) clearly support a Co^{2+} state in the Mo/Co compound. Figure 2 shows the Mo-L₃ edges for a series of Mo-standards along with $La_5Mo_4O_{16}$ samples in powder form and crystal-platelet-oriented-collage form, with the photon polarization vector in the platelet (ab) plane. The Mo-L₃ transitions involve empty Mo-d final states and therefore provide a probe of the empty d-density-of states (modified by matrix element and atomic multiplet effects). The A and B features of MoO₃ (for example) are respectively associated with t_{2g} and e_g Mo-d final states. The spectral signatures of increasing Mo-valence are an $A(t_{2g})$ -feature increases with and a chemical shift to higher energy of the centrum of the A-B feature group. The overall Mo-L₃ spectrum supports a Mo valence (averaged over all sites) well above 4+ but less than 5+. The oriented crystal spectrum is sensitive to d-orbital hole states oriented in the crystallographic ab-plane and manifests a much sharper crystal field splitting.

Comparison of the Mo-L₃ edges for powdered samples of $La_5Mo_4O_{16}$ and $La_5Mo_3CoO_{16}$ (Figure 3) reveals that the Co substituted compound manifests a dramatically sharper, more intense A-feature and an overall shift to higher energy. This is consistent with the Mo-valence increase expected upon Co^{2+} substitution. Oriented crystal XAS measurements indicate a strong in-ab-plane character for the Co-induced Mo-d holes.

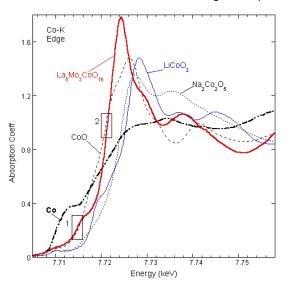


Figure 1

5

Mo-L₃

Edge

La₃Mo₄O₁₆ powder

A

La₃Mo₃CoO₁₆ powder

1

0

2515

2520

2525

Energy (eV)

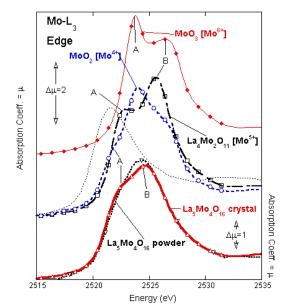


Figure 2

Figure 3